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KNOCK RATINGS OF GASOLINE SUBSTITUTES

By Afton D. Puckett

ABSTRACT

Knock ratings of gaseous paraffins and olefins through C_4, and of carbon monoxide, were determined by current motor and aviation test methods. Auxiliary apparatus and modifications of test engines necessary to rate gases are described.

Antiknock qualities of ethyl and normal butyl alcohol and acetone, both alone and in blends, were determined by current motor-fuel rating procedures. Blending characteristics of these materials with straight run gasolines and naphthas were investigated.

Diethyl ether in ethyl alcohol blends showed a high positive sensitivity (Coordinating Fuel Research Committee (CFR) research minus American Society for Testing Materials (ASTM) motor octane number) for ether concentrations below 48 percent and a high negative sensitivity above that figure. The tests indicated that blends containing up to 45 percent of ether should give relatively knock-free performance under conditions of steady operation.

CONTENTS

I. INTRODUCTION

As part of a program of investigation of the properties of various substitutes for gasoline as a fuel for internal-combustion engines, knock ratings were determined on a number of compounds and blends. The primary purpose of the major investigation was to ascertain whether, and to what extent, substitutes that could be produced in certain areas where petroleum products were scarce or entirely lacking could be used successfully. With this end in view, the antiknock qualities of a number of materials, both gaseous and liquid, were determined by the current CFR Research (CRC Designation F–1) the ASTM Motor D 357 (CRC Designation F–2), and the ASTM Aviation D 614 (CRC Designation F–3) methods. Included to give as complete information as possible were a number of hydrocarbon gases ordinarily obtained from petroleum that obviously do not fall into the category of easily available gasoline substitutes.

Reliable knock ratings by current methods are presented that either were not hitherto reported in the literature, or, in some cases, were of questionable precision because of outmoded methods of test or other irregularities.

II. METHODS OF TEST

The unit currently approved for the knock rating of both motor and aviation gasolines has been designed and built to the specifications of the Cooperative Fuel Research Committee. It is a single-cylinder engine, belt connected to a synchronous motor generator, which maintains constant speed. Compression ratio is continuously variable between 4 and 10 and may be changed while the engine is operating.[1]

The CFR Research (CRC F–1), ASTM Motor (ASTM D 357, CRC F–2), and the ASTM Aviation (ASTM D 614, CRC F–3) methods differ in instrumentation and engine operating conditions. The F–1 and F–2 methods make use of a bouncing pin and knockmeter to detect and indicate knock intensity, whereas the F–3 method utilizes a standard thermocouple, or "thermal plug", and potentiometer to differentiate between knocking tendencies of the fuels. Engine operating conditions for the three methods are shown in table 1.

All determinations of antiknock quality of the liquid fuels tested were made in strict accordance with the standard test methods and on standard knock-test units. Before each run the engines were

TABLE 1.—*Engine operating conditions for standard methods of knock rating*

Test method	CFR research	ASTM motor	ASTM aviation
ASTM designation		D 357	D 614.
CRC designation	F–1	F–2	F–3.
Intake air temperature, ° F	125±2	75 to 125	125 ±5.
Mixture temperature, °F		300 ±2	220 ±2.
Coolant temperature, ° F	[a] 209 to 215	[a] 209 to 215	374 ±9.
Oil temperature, ° F			150 ±10.
Intake air humidity, grains per pound of dry air.	[b] 25 to 50	[b] 25 to 50	[b] 25 to 50.
Mixture ratio	Maximum knock	Maximum knock	Maximum knock.
Knock intensity [c]	Standard, specified by guide table.	Standard, specified by guide table.	Adjusted so that cp benzene is equal in thermal plug temperature to 87 octane number reference fuel.
Engine speed, rpm	600 ±6	900 ±9	1200 ±12.
Compression ratio	Variable with octane number.	Variable with octane number.	Variable with octane number.
Spark advance, °btc	13, fixed	Variable with compression ratio.	35, fixed.

[a] Constant to within 1° F.

[b] Usually controlled at 27 grains per pound of dry air by passing the intake air through an ice-packed humidity control tower of standard design.

[c] Standard knock intensity for the F–1 and F–2 methods is defined as that obtained with a blend of isooctane and normal heptane under the standard conditions of the methods and at a compression ratio corresponding to the blend used and to the prevailing barometric pressure in accordance with the standard knock intensity guide tables for the respective method; for the F–3 method the knock intensity is set by operating at a compression ratio to give a thermal-plug temperature in accordance with a "match temperature line" determined at the beginning of each day's testing.

[1] For detailed descriptions of the test appartaus and procedures see CRC Procedures F–1–1044, F–2–1044, and F–3–1044, Coordinating Research Council, 30 Rockefeller Plaza, New York 20, N. Y.; or ASTM Methods D 357 and D 614, ASTM Book of Standards, 1944, Part III, NonMetallic Materials, American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa.

carefully checked and adjusted to give proper ratings on standardization fuels of known octane number. However, as the standard engines are not normally equipped to operate on gaseous fuels, it was necessary to modify the carburetors in order to obtain ratings on the gases tested. A connection was installed on the standard air-intake elbow of the carburetor, so that gas could be introduced into the air stream ahead of the venturi. To rate the gas samples, the carburetor fuel selector valve was turned to an "off" position, and the gas was admitted through this connection. By using this system, satisfactory engine operation was obtained, there was a minimum of deviation from either standard equipment or conditions, and the usual bracketing procedure was followed.

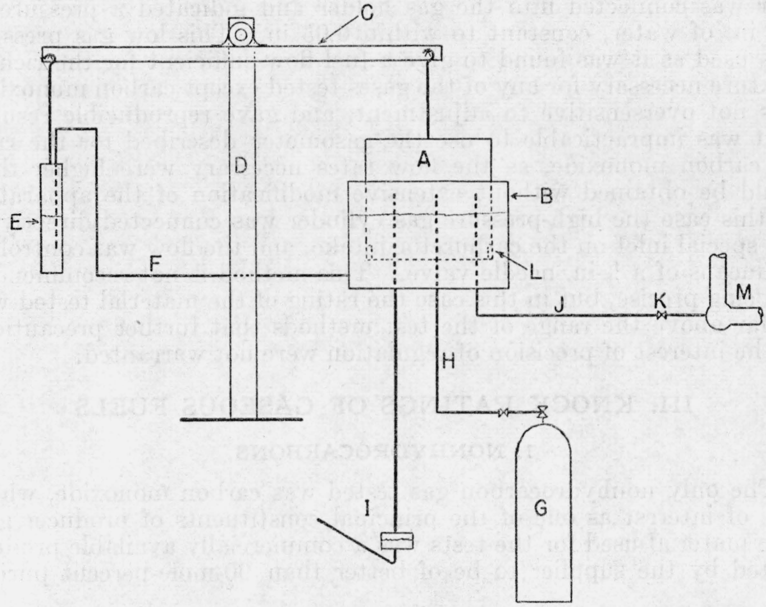

FIGURE 1.—*Constant pressure gasometer.*

A, Gasholder; *B*, water tank; *C*, ball-bearing-mounted beam; *D*, beam support; *E*, counterbalance bucket; *F*, siphon line; *G*, high-pressure gas cylinder; *H*, gas cylinder to gasometer connection; *I*, inclined single-leg manometer; *J*, gas line to engine; *K*, gas-throttling valve; *L*, lead weights; *M*, CFR carburetor air intake.

The F–1, F–2, and F–3 methods require that fuels be tested at the fuel-air ratio for maximum knock. Prerequisite to this condition is a rate of fuel flow which may be varied to give mixtures appreciably richer and appreciably leaner than that for maximum knock, and once set will remain constant long enough for the engine to reach equilibrium. These requirements were fulfilled by the use of the gasometer illustrated schematically in figure 1. The gas from cylinder *G* was led through line *H* into gas holder *A*, which was weighted with lead strips *L*, and thence through line *J* to the intake elbow *M*. *J* consisted of a section of ⅜-in. outside diameter copper tubing into *A* and a section of ⅜-in. inside diameter rubber tubing from the copper tube to the engine inlet connection. It was originally intended that *K* should be a standard ¼-in. globe valve, but such a valve was found to offer excessive resistance to flow. Consequently a screw-clamp-

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type hose cock was tried and found to give excellent regulation. The gas holder was suspended on a knife edge from beam *C*, which was pivoted at its center on a ball bearing mounted on column *D*. A small bucket, *E*, also suspended from the beam opposite the gas holder, acted as a counterbalance. Line *F* was installed as a siphon from the water tank *B* and extended down into the counterbalance bucket thus maintaining equal liquid levels in the two. The cross-sectional area of *E* was such that any change in the submerged volume of the walls of *A*, and consequently of the buoyant force acting on the gas holder, was compensated by the change in the amount of water in *E*, and constant pressure was maintained in the gas holder regardless of its position. The inclined single-leg manometer was connected into the gas holder and indicated a pressure of 1.2 in. of water, constant to within 0.05 in. This low gas pressure was used as it was found to give a fuel flow sufficient for the richest mixture necessary for any of the gases tested except carbon monoxide, was not oversensitive to adjustment, and gave reproducible results.

It was impracticable to use the gasometer described for the runs on carbon monoxide, as the flow rates necessary were higher than could be obtained without extensive modification of the apparatus. In this case the high-pressure gas cylinder was connected directly to the special inlet on the carburetor intake, and the flow was controlled by means of a ⅛-in. needle valve. This method is not recommended as being precise, but in this case the rating of the material tested was so far above the range of the test methods that further precautions in the interest of precision of regulation were not warranted.

III. KNOCK RATINGS OF GASEOUS FUELS

1. NONHYDROCARBONS

The only nonhydrocarbon gas tested was carbon monoxide, which was of interest as one of the principal constituents of producer gas. The material used for the tests was a commercially available product stated by the supplier to be of better than 90-mole-percent purity.

TABLE 2.—*Knock ratings of gaseous fuels*

Fuel	Test method (CRC designation)		
	F-1	F-2	F-3
Nonhydrocarbon:			
Carbon monoxide (90+mole%)	[a]>6	[a]>6	[a]>6
Hydrocarbon:			
Paraffin—			
Methane (99+mole%)	[a]>6	[a]>6	[a]>6
Ethane (99+mole%)	[a] 4.6	.05	99.0
Propane (99+mole%)	[a] 1.9	97.1	[a].08
n-Butane (99+mole%)	93.6	90.1	93.0
Isobutane (99+mole%)	[a].17	97.6	[a].02
Olefin—			
Ethylene (USP anesthesia grade)	[a].03	75.6	([b])
Propylene (99+mole%)	[a].24	84.9	77.5
Butene-1 (99+mole%)	97.4	81.7	74.9
Butene-2 (99+mole%)	99.6	86.5	76.2
Isobutylene (95+mole%)	[a].26	88.1	87.6

[a] TEL in isooctane, ml/gal.

[b] Ethylene could not be rated under the standard F-3 conditions. Ratings made at thermal-plug temperatures considerably above that prescribed by the method gave values of 70 and 74 octane number.

From the extremely high knock ratings listed in table 2, it is evident that as far as antiknock quality is concerned, the gas could be used with supercharge and in high-compression engines.

2. HYDROCARBONS

The normally gaseous paraffins and olefins rated were commercially available samples stated to be of the purity indicated in table 2. In any case where there was reason to question the precision of a rating, duplicate tests were run and an average value listed in the table.

IV. NONHYDROCARBON BLENDS

Liquid substitute fuels considered were ethyl alcohol, both 190- and 200-proof; acetone; normal butyl alcohol; and diethyl ether (all of technical grade). Ether, although known to be of very low octane number, was included in the list because of the possibility of its use to improve volatility characteristics of the other fuels.

1. ETHYL ALCOHOL-DIETHYL ETHER BLENDS

Both ASTM motor and CFR research octane numbers were determined on a series of ethyl alcohol-diethyl ether blends in order to ascertain how much ether could be added without reducing knock rating to objectionably low values. Knock ratings obtained for the blends are listed in table 3 and are plotted against composition in figure 2. Behavior of the blends is somewhat unusual in that decrease in octane number with increasing ether content becomes very rapid in the neighborbood of 45 percent by volume of ether and that for low concentrations of ether the sensitivity (difference between CFR research and ASTM motor octane numbers) is positive and high, whereas at concentrations of ether above 48 percent exactly the oppo-

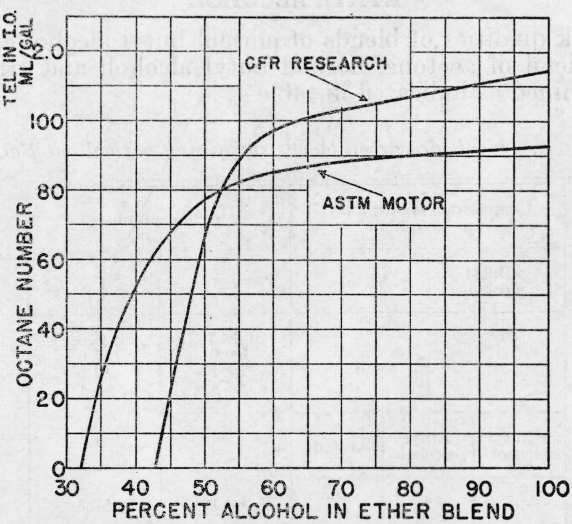

FIGURE 2.—*CFR research and ASTM motor method octane numbers of blends of 200-proof ethyl alcohol with diethyl ether.*

site is true. These tests indicate that blends of alcohol and ether containing as high as 45 percent of ether should give freedom from knock under conditions of steady operation. Road tests, however, have shown that blends containing 25 percent or more of ether will knock violently for one or two cycles if the throttle is opened quickly for rapid acceleration.

TABLE 3.—*CFR research and ASTM motor octane numbers of alcohol-ether blends*

Composition of blend, percent, by volume		Octane number	
200-proof alcohol	Diethyl ether	F-1	F-2
100	0	[a] 1.4	92.2
85	15	[a] .88	90.0
70	30	[a] .34	88.3
60	40	97.9	85.2
55	45	89.8	82.3
50	50	66.2	74.4
45	55	29.9	70.4
42.9	57.1	0	
40	60	------------	52.0
32	68	------------	0
190-proof alcohol	Diethyl ether		
100	0	[a] 2.7	93.8
70	30	[a] .60	89.2
50	50	91.1	83.8
40	60	------------	45.0
35	65		10.9
33.4	66.6		0

[a] TEL in isooctane, ml/gal.

2. BLENDS CONTAINING *n*-BUTYL ALCOHOL, ACETONE, AND ETHYL ALCOHOL

Antiknock qualities of blends of normal butyl alcohol and acetone and of a blend of acetone, normal butyl alcohol, and ethyl alcohol were determined as indicated in table 4.

TABLE 4.—*Nonhydrocarbon blends containing normal-butyl alcohol*

Composition of blend, percent by volume			Octane number	
n-Butyl alcohol		Acetone	F-1	F-2
100		0	99.5	85.6
71.5		28.5	100.0	87.0
50		50	[a] .17	89.5
0		100	[a] 3.4	[a] 3.1
n-Butyl alcohol	Ethyl alcohol	Acetone		
67	6	27	[a] 0.12	87.7

[a] TEL in isooctane, ml/gal.

V. HYDROCARBON FUELS CONTAINING NONHYDROCARBON COMPONENTS

1. GASOLINE BLENDS

To determine the practicability of extending supplies where some petroleum was available, fuels made up of varying amounts of ethyl alcohol, acetone, and/or normal butyl alcohol in gasoline or blending naphthas were investigated. Preliminary work along this line consisted of determining knock ratings by motor method of samples of 40, 50, and 60 octane number standard secondary reference fuels containing up to 40 percent by volume of alcohol. One object of these particular tests was to obtain an estimate of how much alcohol would have to be added to straight-run gasolines of 40, 50, or 60 octane number to bring their knock rating up to that of regular grade (70 ASTM motor octane number) fuel. As can be seen from the curves in figure 3, blends of these fuels containing 30, 20, and 12 per-

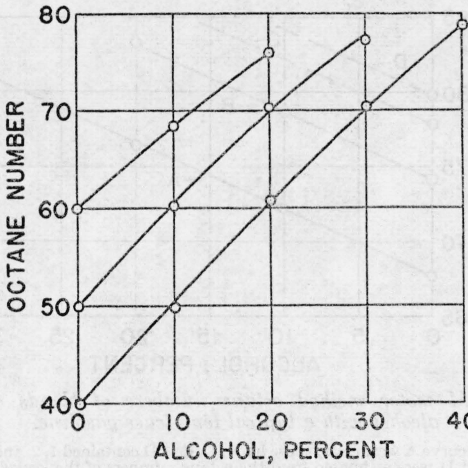

FIGURE 3.—*ASTM motor method octane numbers of blends of 200-proof ethyl alcohol with 40, 50, and 60 octane number standard reference fuels.*

cent of alcohol, respectively, met this requirement. Over the range of concentration investigated the use of alcohol in these fuels resulted in an average increase in knock rating of 1.0 octane number in the 40 and 50 octane number fuels and an average increase of 0.8 octane number in the 60 octane number fuel for each 1-percent increment of alcohol. Knock ratings of each of the blends tested are shown in table 5.

TABLE 5.—*Knock ratings of 200-proof ethyl alcohol-standard reference fuel blends*

Alcohol in blend, percent by volume	ASTM motor octane number		
0	40.0	50.0	60.0
10	49.8	60.2	68.4
20	60.8	70.3	75.9
30	70.4	77.2	----------
40	78.7	----------	----------

Tests were made by the motor method on a straight-run gasoline, typical of that furnished by a Texas Gulf Coast Refinery for nonmilitary use under lend-lease commitments, to determine the saving of tetraethyl lead that might result from the use of alcohol to raise the knock rating to that of a regular or a premium grade fuel. Results indicated that this material could be leaded to 70 and to 75 motor octane number with 0.25 and 1.1 milliliters of tetraethyl lead per gallon, respectively, and that the same ends could be accomplished through the use of blends containing 5.0 and 16.3 percent of alcohol in the finished products. On the basis of these data, it appeared feasible to ship this gasoline to countries requiring fuels of these octane numbers and possessing the alcohol with which to make the blends. Thus could be effected a saving in lead, and at the same time a reduction, by the amount of the alcohol used, in the tanker capacity needed. Properties of the gasoline and knock ratings of the alcohol blends are shown in table 6 and figure 4, respectively.

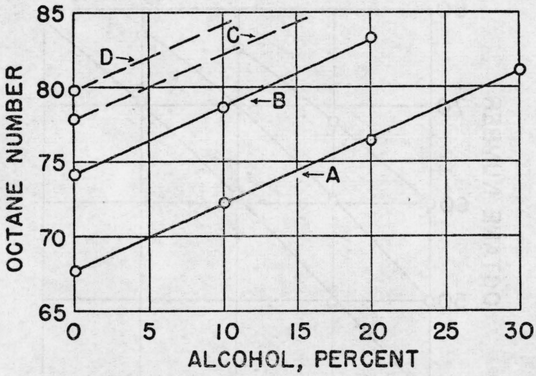

FIGURE 4.—*ASTM motor method octane numbers of blends of 200-proof ethyl alcohol with a typical lend-lease gasoline.*

Samples represented by curve A were clear, those by B, C, and D contained 1, 2, and 3 ml TEL/gal, respectively. Curves C and D were estimated from the octane numbers of the leaded gasoline and the slope of A and B.

TABLE 6.—*Lend-lease gasoline, inspection data*

Distillation:	
Initial boiling point, ° F	100
10% distilled, ° F	124
50% distilled, ° F	244
90% distilled, ° F	343
End point, ° F	381
Recovery, %	96.5
Loss, %	2.4
Residue, %	1.1
Reid vapor pressure, lb./in.²	10.0
ASTM gum	Trace
Sulfur, %	0.065
ASTM motor octane number:	
Clear	67.7
Leaded 1.0 ml. TEL/gal	74.2
Leaded 2.0 ml. TEL/gal	77.9
Leaded 3.0 ml. TEL/gal	79.8

Tests similar to the preliminary runs on alcohol–reference fuel blends were made on acetone–reference fuel blends, as indicated in table 7 and figure 5.

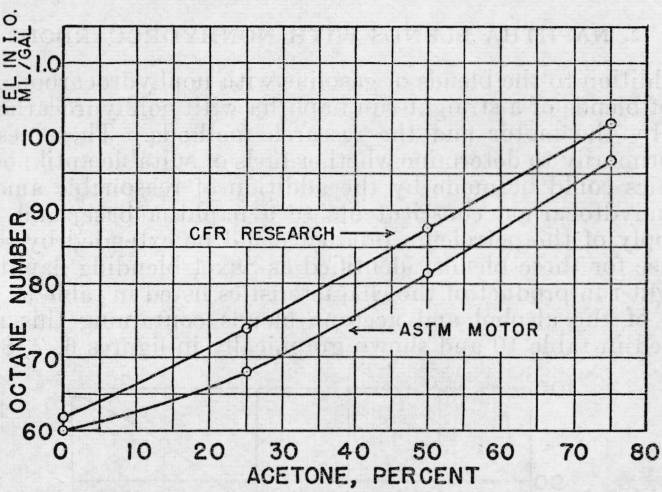

FIGURE 5.—*CFR research and ASTM motor method octane numbers of blends of acetone with a 60-motor octane number standard reference fuel.*

TABLE 7.—*Knock ratings of acetone–reference fuel blends*

Composition of blend, percent by volume		Octane number	
Acetone	Standard reference fuel (52% C-12/A-6)	F-1	F-2
0	100	61.7	60.0
25	75	73.8	68.0
50	50	87.5	81.4
75	25	[a] .18	96.7

[a] TEL in isooctane, ml./gal.

The effect of the addition of alcohol and acetone to an Australian shale-oil motor fuel was studied, as indicated in table 8.

TABLE 8.—*Properties of Australian shale oil motor fuel*

Gravity, deg API	58.5
Reid vapor pressure, lb/in^2	7.0
Distillation:	
Initial boiling point, ° F	99
10% distilled, ° F	149
50% distilled, ° F	255
90% distilled, ° F	342
End point, ° F	378
Sulfur, %	0.20
Corrosion	Negative
ASTM gum, mg/100 ml	2
Bromine number, mg/100 g	78.6

Knock rating:

	Octane number					
	F-1			F-2		
TEL content, ml/gal	0	1	4	0	1	4
Shale-oil motor fuel	74.6	80.2	86.1	69.9	72.0	76.9
50% alcohol blend				83.0		85.4
25% acetone blend				76.9		82.3
50% acetone blend				84.0		90.7

2. NAPHTHA BLENDS WITH NONHYDROCARBONS

In addition to the blends of gasoline with nonhydrocarbons, several series of blends of a straight-run naphtha with nonhydrocarbons were tested by the motor and the research methods. These tests were made primarily to determine whether fuels of suitable antiknock characteristics could be made by the addition of reasonable amounts of the nonhydrocarbon constitutents to a naphtha base, and how far the supply of the petroleum product could be extended by so doing. The base for these blends, identified as Saxet blending naphtha, was a straight-run product of the characteristics listed in table 9. Knock ratings of the alcohol and acetone blends containing this material are listed in table 10 and shown graphically in figures 6, 7, 8, and 9.

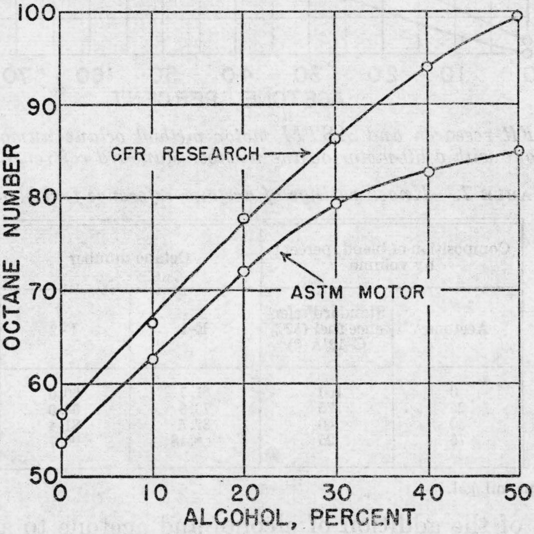

FIGURE 6.—*CFR research and ASTM motor method octane numbers of blends of 200-proof ethyl alcohol with Saxet naphtha.*

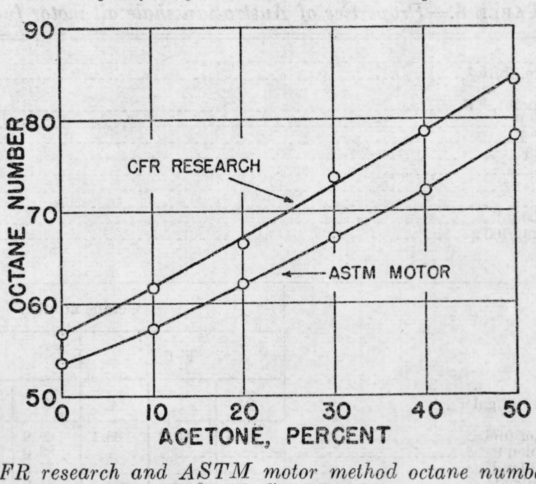

FIGURE 7.—*CFR research and ASTM motor method octane numbers of blends of acetone with Saxet naphtha.*

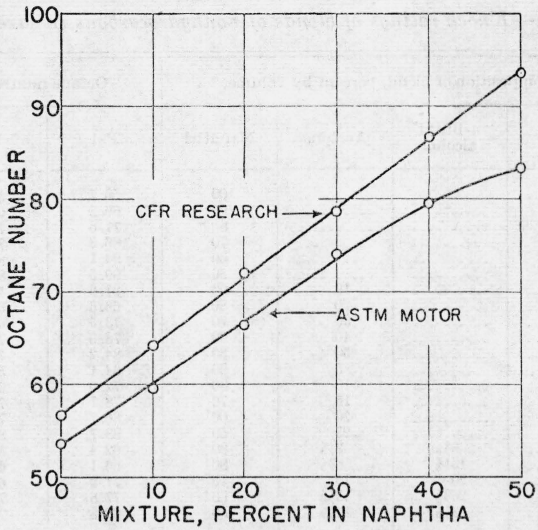

FIGURE 8.—*CFR research and ASTM motor method octane numbers of blends of a mixture of equal volumes of 200-proof alcohol and acetone with Saxet naphtha.*

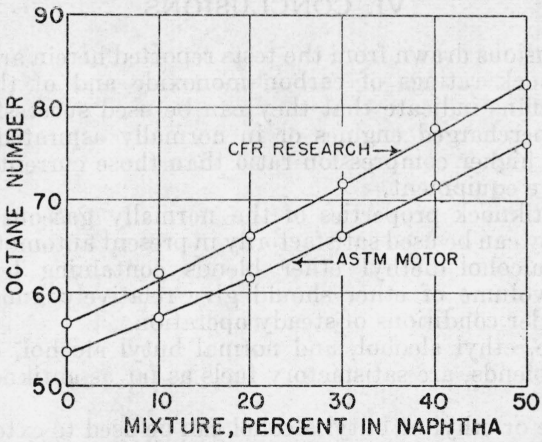

FIGURE 9.—*CFR research and ASTM motor method octane numbers of blends of a mixture of two volumes of n-butyl alcohol and one volume of acetone with Saxet naphtha.*

TABLE 9.—*Saxet naphtha, inspection data*

Gravity, deg API	55.4
Reid vapor pressure, lb/in.^{2}	3.0
Distillation:	
Initial boiling point, °F	140
5% distilled, °F	176
10% distilled, °F	202
20% distilled, °F	227
30% distilled, °F	246
40% distilled, °F	263
50% distilled, °F	280
60% distilled, °F	295
70% distilled, °F	318
80% distilled, °F	337
90% distilled, °F	360
95% distilled, °F	381
End point, °F	397
Recovery, percent	98.1
Residue, percent	1.0

TABLE 10.—*Knock ratings of blends of nonhydrocarbons in saxet naphtha*

Composition of blend, percent by volume				Octane number	
Ethyl alcohol	n-Butyl alcohol	Acetone	Naphtha	F-1	F-2
----------	----------	----------	100	56.7	53.6
10	----------	----------	90	66.5	62.6
20	----------	----------	80	77.6	72.0
30	----------	----------	70	86.3	79.3
40	----------	----------	60	94.1	82.7
50	----------	----------	50	99.5	85.0
----------	----------	10	90	61.6	57.3
----------	----------	20	80	66.5	62.1
----------	----------	30	70	73.5	67.1
----------	----------	40	60	78.6	72.2
----------	----------	50	50	84.2	78.1
5	----------	5	90	64.1	59.6
10	----------	10	80	72.0	66.5
15	----------	15	70	78.7	74.1
20	----------	20	60	86.7	79.6
25	----------	25	50	93.7	83.4
----------	6⅔	3⅓	90	62.4	57.3
----------	13⅓	6⅔	80	66.1	61.5
----------	20	10	70	71.9	66.1
----------	26⅔	13⅓	60	77.8	71.8
----------	33⅓	16⅔	50	82.8	76.2

VI. CONCLUSIONS

The conclusions drawn from the tests reported herein are as follows:

1. The knock ratings of carbon monoxide and of the normally gaseous paraffins indicate that they can be used successfully as fuel in either supercharged engines or in normally aspirated engines of considerably higher compression ratio than those currently available in automotive equipment.

2. The antiknock properties of the normally gaseous olefins are such that they can be used satisfactorily in present automotive engines.

3. Ethyl alcohol–diethyl ether blends containing less than 45 percent by volume of ether should give relatively knock-free performance under conditions of steady operation.

4. Acetone, ethyl alcohol, and normal butyl alcohol, either separately or in blends, are satisfactory fuels as far as antiknock value is concerned.

5. Acetone or ethyl or butyl alcohol can be used to extend supplies of gasoline or can be blended with suitable petroleum naphthas to make motor fuels of satisfactory knock rating.

6. When up to 30 percent by volume of ethyl alcohol is blended with gasoline of 40 to 60 ASTM motor octane number, the improvement in knock rating is of the order of one octane unit for each percent of alcohol.

7. Acetone, though higher in octane number when tested neat, is less effective in blends than is ethyl alcohol.

WASHINGTON, August 3, 1945.